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Pulsed recording of anisotropy and holographic polarization gratings in azo-polymethacrylates with different molecular architectures

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Recording of anisotropy and holographic polarization gratings using 532 nm, 4 ns light pulses has been carried out in thin films of polymers with the same azobenzene content (20 wt %) and different molecular architectures. Random and block copolymers comprising azobenzene and methylmethacrylate (MMA) moieties as well as statistical terpolymers with azobenzene, biphenyl, and MMA units have been compared in terms of recording sensitivity and stability upon pulsed excitation. Photoinduced anisotropy just after the pulse was significantly higher in the case of the block copolymers than in the two statistical copolymers. The stability of the recorded anisotropy has also been studied. While a stationary value of the photoinduced anisotropy (approximately 50% of the initial photoinduced value) is reached for the block copolymer, photoinduced anisotropy almost vanished after a few hours in the statistical copolymers. Polarization holographic gratings have been registered using two orthogonally circularly polarized light beams. The results are qualitatively similar to those of photoinduced anisotropy, that is, stability of the registered grating and larger values of diffraction efficiency for the block copolymer as compared with the random copolymers. The recording of holographic gratings with submicron period in films several microns thick, showing both polarization and angular selectivity, has also been demonstrated. Block copolymers showed a lamellar block nanosegregated morphology. The interaction among azo chromophores within the nanosegregated azo blocks seems to be the reason for the stability and the photoresponse enhancement in the block copolymer as compared with the statistical ones. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2943260]

INTRODUCTION

The unique response of azobenzene molecules to light stimuli has attracted the attention of scientists and technologists during the last decades.[1–5] The interaction of light with properly engineered azobenzene containing materials has demonstrated to be an effective and elegant tool to modulate their optical and mechanical properties.[6–18] In particular, an intense investigation has been performed on the optical anisotropy induced by polarized light in azobenzene side chain polymers, due to its potential application in reversible optical storage technologies. Linearly polarized light in the blue-green region selectively induces isomerization of azo molecules with their absorption transition dipole moment having a component parallel to the light polarization direction. Due to this selective excitation and to chromophore reorientations during *trans-cis-trans* isomerization cycles, an anisotropic orientational distribution is reached with the long molecular axis of the azo units preferentially oriented perpendicular to the light polarization direction. As a result, a macroscopic optical anisotropy is induced that can be subsequently erased by thermal or optical means making the material reusable.

The photoinduction of anisotropy and different types of holographic gratings has been extensively studied in azobenzene side chain polymers mainly using continuous wave (cw) lasers.[6–15] High and stable values of birefringence have been obtained in liquid crystalline homopolymers with azobenzene side units due to the strong interaction between chromophores.[8,9] In spite of these good properties, the use of these liquid crystalline materials is inherently limited to thin grating recording. This limitation is due to the fact that liquid crystalline microdomains produce light scattering, decreasing the optical quality of films as thickness increases. Transparency is improved by using amorphous materials but, in general, the magnitude and stability of the recorded anisotropy get substantially worse. In addition, thick films of the homopolymers usually have high optical density (several units) at the recording wavelength due to the high concentration of chromophores. This prevents the film to get sensitized in the whole thickness. These drawbacks have already been identified by several authors and different strategies specially focused on the material design have been explored, trying to obtain thick and transparent films while keeping stability and large refractive index modulation.[19–26] Ikeda and co-workers have studied the recording of anisotropy and holographic gratings using cw lasers in statistical terpolymers containing

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azobenzene units together with transparent methyl methacrylate (MMA) and mesogenic transparent moieties, either biphenyl or tolane in the side chain.[19,20] Linearly polarized light acts on the azobenzene units orienting them perpendicular to the polarization direction. Due to the interactions of azobenzene units with the mesogenic nonphotoactive moieties, these last become simultaneously oriented, contributing and stabilizing the anisotropy. Another different strategy to reduce azobenzene concentration while keeping good photo-optical response is to use block copolymers containing one block with azobenzene units and another one made of a polymer that does not absorb at the recording wavelength. A nanosegregation of the two blocks can take place through appropriate processing, and some of the photoinduced properties of the azobenzene homopolymer can be retained within the nanodomains. The recording of stable anisotropy and holographic gratings in these block copolymer materials have been accomplished by several groups using cw light sources.[21–26]

Recording using short light pulses (in the range of nanoseconds to hundreds of femtoseconds) has also been demonstrated to be of relevance for optical applications.[27–38] In particular, the use of 532 nm lasers of few nanosecond pulse duration has shown to be effective in the recording of optical anisotropy and holographic gratings.[31–38] Some of these studies have been carried out in liquid crystalline materials,[31] although most of the work has been done in amorphous polymers. Stationary values of birefringence in the range of 10^{-3} have been reached. Birefringence initially increases just after the pulse, but a relaxation of more than one order of magnitude is usually observed along the time (over periods ranging from seconds to several hours).[31,36] Different types of holographic gratings (using intensity and polarization patterns) have also been recorded in amorphous azobenzene containing polymers using 532 nm nanosecond light pulses.[32–36] Although some contribution to the diffraction efficiency has been associated with bulk anisotropy, the relief contribution is usually dominant even when polarization patterns are employed in the recording.[33] This surface relief contribution prevents the use of this recording protocol in many optical storage applications.[34] Recently, a study has been carried out in our group on the recording of birefringence and holographic gratings in a liquid crystalline side chain polymethacrylate with azobenzene pendant units using 532 nm, 4 ns light pulses.[37,38] Stable values of birefringence of about 10^{-2} were reached for certain irradiation conditions, and stable polarization gratings with efficiencies of about 0.8% with no relief contribution were obtained for thin films (around 1 μm) by using one single pulse. Unfortunately, the use of these materials is limited to the recording of thin gratings for the reasons mentioned above (liquid crystal microdomains and large optical density in few microns thick films). As in the case of cw recording, new materials need to be explored in order to fulfill optical storage application requirements.

In this paper, we present a comparative study of the recording of photoinduced anisotropy and holographic polarization gratings using 532 nm, 4 ns light pulses, in three azobenzene side chain polymers with the same diluted azobenzene content but different molecular architectures. Random and block copolymers comprising azobenzene photoactive units and MMA as well as statistical terpolymers with azobenzene, biphenyl, and MMA have been compared in terms of recording sensitivity and stability upon pulsed excitation. Better photoresponse is found in the block copolymer showing larger and more stable values of photoinduced anisotropy and diffraction efficiency in films of similar thickness. The recording of Bragg gratings in thick films of the block copolymer using light pulses is also explored.

EXPERIMENTAL

The chemical structure of the polymers used in this study is shown in Fig. 1. In all the cases the azobenzene content was around 20% weight. The random copolymer and terpolymer (ran-PMMA-Azo20 and TER20 respectively) were synthesized by conventional free radical polymerization, while the block copolymer PMMA-Azo20 was synthesized by atom transfer radical polymerization, according to the method published elsewhere.[25] The structure, nomenclature, and composition of the polymers are given in Fig. 1, while thermal properties, molecular weights, and polydispersity are summarized in Table I. Transition temperatures of the polymers were determined by differential scanning calorimetry (DSC) using a DSC Q-1000 from TA Inst under a nitrogen atmosphere. Thermal stability was checked by thermogravimetry. All the copolymers showed a good thermal stability up to 200 °C and a sharp decomposition with an onset around 300 °C. Molecular weights of the statistical copolymers were characterized by gel permeation chromatography (GPC) using polystyrene standards. In the case of the block copolymer, the molecular weight was calculated taking into account the molar ratio of repeating units detected by NMR and the previously determined length of polymethyl methacrylate (PMMA) block calculated by GPC using THF as solvent and PMMA standards.

Films for optical measurements were prepared by casting from a solution of the polymers in propylene glycol methyl ether acetate onto clean glass substrates. Film thickness, as well as surface film relief, was measured using a DEKTAK profilometer. Before performing any experiment, films were heated up to 150 °C for 30 min and then cooled down to room temperature (RT). Optical absorption was measured using a Varian Cary 500 UV-visible-IR spectrophotometer.

Photoinduced anisotropy measurements were carried out in the setup shown in Fig. 2(a). The linearly polarized 532 nm light from the second harmonic of a pulsed (4 ns pulses) Nd:YAG (yttrium aluminum garnet) laser was used as the exciting light. The sample was placed between crossed polarizers with their polarization directions at $\pm 45°$ with the vertical axis. The light from a 780 nm diode laser (30 mW) transmitted through the polarizer-sample-polarizer system was measured with an amplified Si *p-i-n* photodetector (Thorlabs PDA10A-EC, bandwidth of 150 MHz). It has been checked that the 780 nm light does not introduce any changes in the photoinduced anisotropy values. The transmitted light intensity I is given by Eq. (1),[38]

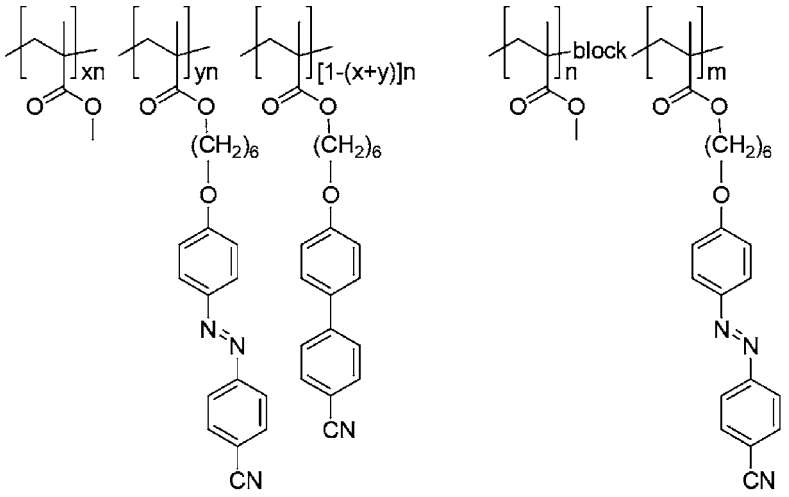

FIG. 1. Structure and composition of the statistical copolymers ran-PMMA-Azo20 and TER20 and the block copolymer PMMA-Azo20.

Nomenclature	Composition		Azo Content	
	x	y	% mol	% wt
ran-PMMA-Azo20	0.94	0.06	6	20
TER20	0.85	0.07	7	20
PMMA-Azo20			6	20

$$I = I_o \sin^2\left(\frac{\pi|\Delta n|d}{\lambda}\right), \tag{1}$$

where I_o is the intensity transmitted by the as quenched films between parallel polarizers, Δn is the photoinduced birefringence, d is the film thickness, and λ is the wavelength of the measuring light (780 nm).

The setup used for polarization holographic recording and diffraction efficiency measurements is shown in Fig. 2(b). The 532 nm light from the second harmonic of a pulsed (4 ns pulses) Nd:YAG laser was divided into two equal intensity orthogonally circular polarized beams (obtained by inserting properly oriented quarter-wave plates) which were made to interfere on the film. The angle between the two interfering beams was 6°, giving a polarization grating pattern with a period (Λ) of approximately 5 μm. The selectivity of the grating for circularly polarized light, characteristic of this type of gratings, was checked by using left and right 780 nm circularly polarized beams.[39] The time evolution of the diffraction efficiency was measured using the circularly polarized 780 nm light and the Si *p-i-n* photodetector. The diffraction efficiency in the first order maximum is given by Eq. (2),[39]

$$\eta_{+1} = \sin^2\left(\frac{\pi|\Delta n|d}{\lambda}\right). \tag{2}$$

Gratings with submicron periods were also recorded in the same holographic setup but changing the angle between the two interfering beams. The usual criterion to consider a holographic grating as a volume one is that the parameter Q given by Eq. (3),

$$Q = \frac{2\pi\lambda d}{n\Lambda^2}, \tag{3}$$

has to be bigger than 10 (see, for example, Ref. 40). In this equation, λ is the vacuum wavelength of the measuring light, d the hologram thickness, n the refractive index of the polymer, and Λ the grating period. A grating period of 700 nm was set for this type of hologram recording. The angular selectivity was checked by measuring the diffracted light intensity while rotating the film around the Bragg angle around

TABLE I. Molecular weights and transition temperatures of the studied polymers.

Nomenclature	Mw[a]	Mw/Mn[b]	Transition temperatures (°C)[c]
ran-PMMA-Azo20	17 500	2.2	*g* 110 *I*
TER20	27 900	2.0	*g* 95 *I*
PMMA-Azo20	25 800	1.18	g_1 62 g_2 97 S_A 149 *I*

[a]Calculated by GPC using THF as solvent and PS standards.
[b]Calculated taking into account the molar ratio of repeating units detected by NMR and the previously determined length of PMMA block calculated by GPC using THF as solvent and PMMA standards.
[c]T_g determined from the second DSC heating scan at 5 °C/min except T_{g1} that was only detected in the first DSC heating scan.

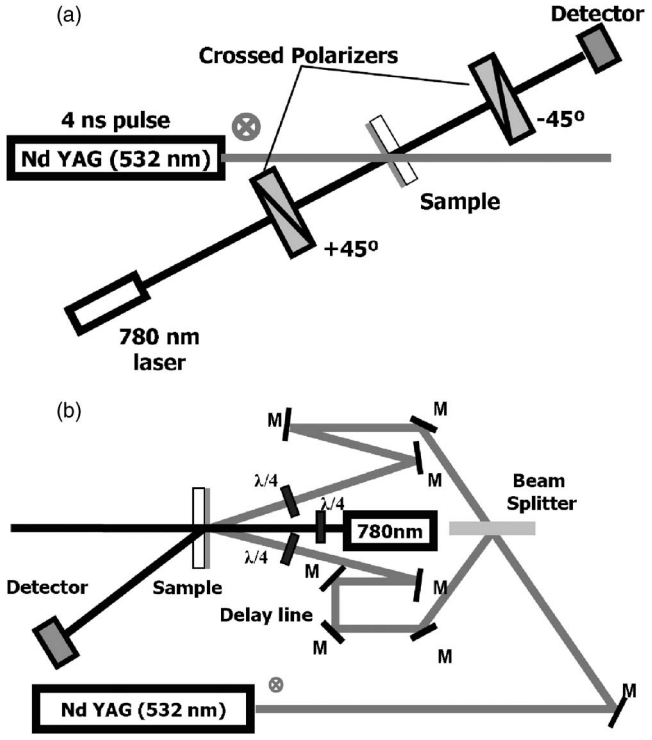

FIG. 2. Experimental setup for (a) photoinduced anisotropy measurements and (b) holographic polarization gratings recording and diffraction efficiency measurements.

an axis perpendicular to the incidence plane of the 532 nm light.

To erase photoinduced anisotropy and holographic gratings, films were heated up to 130 °C for 1 min and then fast quenched to RT. Films treated in this way could be reused and showed reproducible behavior with respect to birefringence and holographic recording.

Samples for transmission electron microscopy (TEM) were prepared as follows: A piece of a few milligrams was introduced into an epoxy resin. After curing and annealing at 130 °C, slices of about 100 nm were cut with a Leica ultramicrotome EM UC6 equipped with a diamond knife (Diatome Ultra 35°) and picked up on carbon coated copper grids. To enhance the contrast between the methyl methacrylate and the azobenzene blocks, the slices were exposed to RuO_4 vapor for 1 h. TEM was measured using a JEOL-2000 FXIII electron microscope.

EXPERIMENTAL RESULTS AND DISCUSSION

The thermal characterization demonstrated that the block copolymer had a liquid crystalline character while random copolymers did not showed liquid crystallinity. X-ray diffraction measurements demonstrated some smectic ordering in the block copolymer. A lamellar nanostructure of the azobenzene block copolymer has been observed in annealed samples (at 130 °C) of the block copolymer by TEM as can be seen in Fig. 3. On the other hand, no defined structure has been observed in the two random copolymers. The block segregation is also supported by DSC data. Two glass transitions at temperatures corresponding to those of the azobenzene and PMMA homopolymers were detected in the first

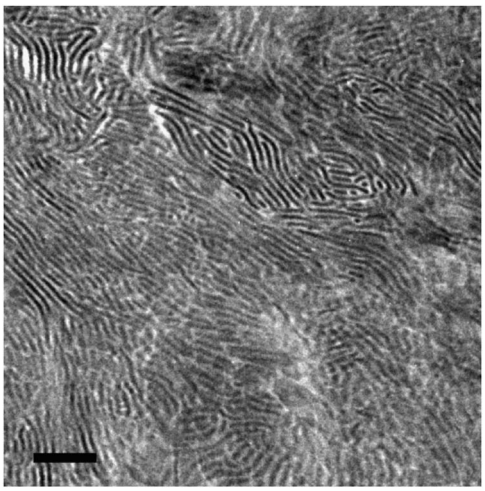

FIG. 3. TEM image of an ultrathin section (100 nm thick) of the block copolymer PMMA-Azo20 showing a lamellar structure. The scale bar is 200 nm.

heating DSC scan. An endothermic transition at around 150 °C corresponding to the smectic A mesophase to isotropic transition of the azobenzene block was observed.[25]

Films for optical measurements were prepared and thermally treated using the method described above. We give in Fig. 4 the UV-visible absorption spectra of the three copolymers. The three spectra show the same features: a main absorption band, at about 365–370 nm, together with a shoulder in the 450 nm region associated with the π-π^* and n-π^* transitions of the *trans* azo moiety, respectively. In addition, the terpolymer TER20 shows a strong absorption below 330 nm due to the presence of the biphenyl moiety. The optical density (OD) of the three films at the 365–370 nm maximum was around 2.2–2.6 corresponding to thicknesses of 1.5–1.8 μm. The OD of the films at the recording wavelength was below 0.03, and therefore nearly homogeneous irradiation in the whole depth of the film was achieved (no recording beam attenuation).

The typical time evolution of 780 nm light intensity transmitted through the polarizer-film-polarizer system [Fig. 2(a)] after irradiation with a single pulse (4 ns, ~500 mJ/cm^2) of linearly polarized 532 nm light is shown in Fig. 5. A sharp increase of the transmitted intensity is observed (for the three polymers) just after the exciting pulse. This increase in transmitted intensity, that is proportional to $|\Delta n|^2$ for low $|\Delta n|$ values [see Eq. (1)], is associated with an increase of the birefringence photoinduced in the material. The inset in Fig. 5(c) shows the same time evolution but in the nanosecond range for the block copolymer film. It can be seen that the induction time of the photoinduced anisotropy is at most 10 ns. We want to point out that the photoinduced Δn is much bigger in the block copolymer than in the two random copolymers for any recording pulse energy (3.3×10^{-3} for the block copolymer and 0.7×10^{-3} for the two random copolymers using the recording energy that maximizes Δn). Measurements in the nanosecond range were also performed in the random copolymers; however, the signal was not intense enough to appreciate the change in the transmitted intensity of measuring light at this time scale

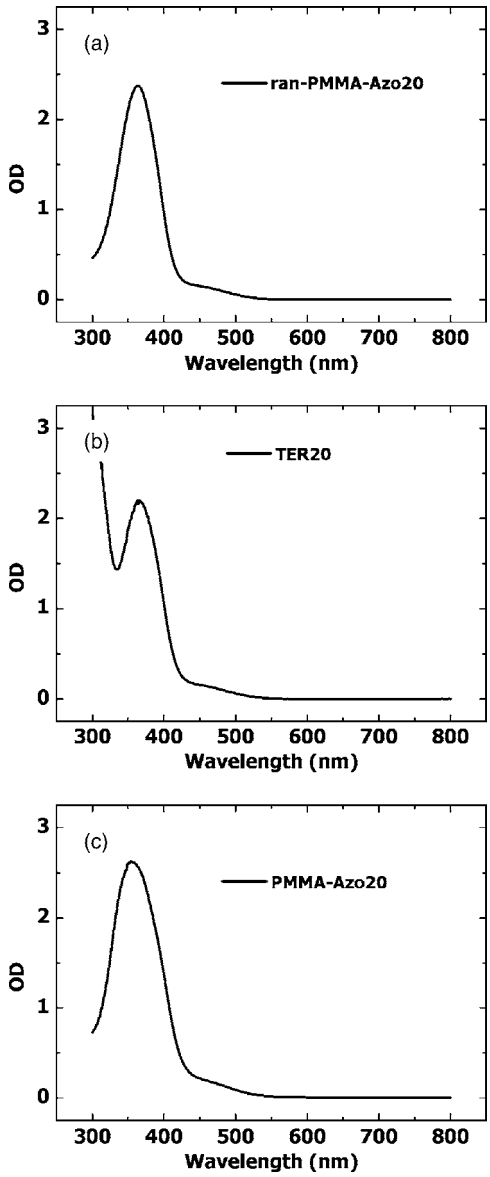

FIG. 4. Optical absorption spectrum of the three copolymers.

(due to the electronic noise) and therefore these results are not included. It is also possible to see in Fig. 5 that the transmitted intensity in the block copolymer is stable within measurement time while a slight decrease is observed for the statistical copolymers. A similar behavior (larger and more stable response for the block copolymer) was observed in a previous study carried out in our laboratory on the anisotropy photoinduced in the same polymers using cw light at 488 nm, but the effect is more remarkable using nanosecond pulsed light.[26] The transmitted intensity, measured 1 s after the pulse and normalized for each polymer to its maximum value (corresponding to the recording energy that maximizes Δn), is plotted in Fig. 6 for different recording energies. For low energy pulses, photoinduced anisotropy increases with increasing light pulse recording energy. An optimum recording energy at about 400–600 mJ/cm^2 is found for the three polymers. Above this optimum energy, photoinduced anisotropy decreases as pulse energy increases.

We have also studied the long term stability of the

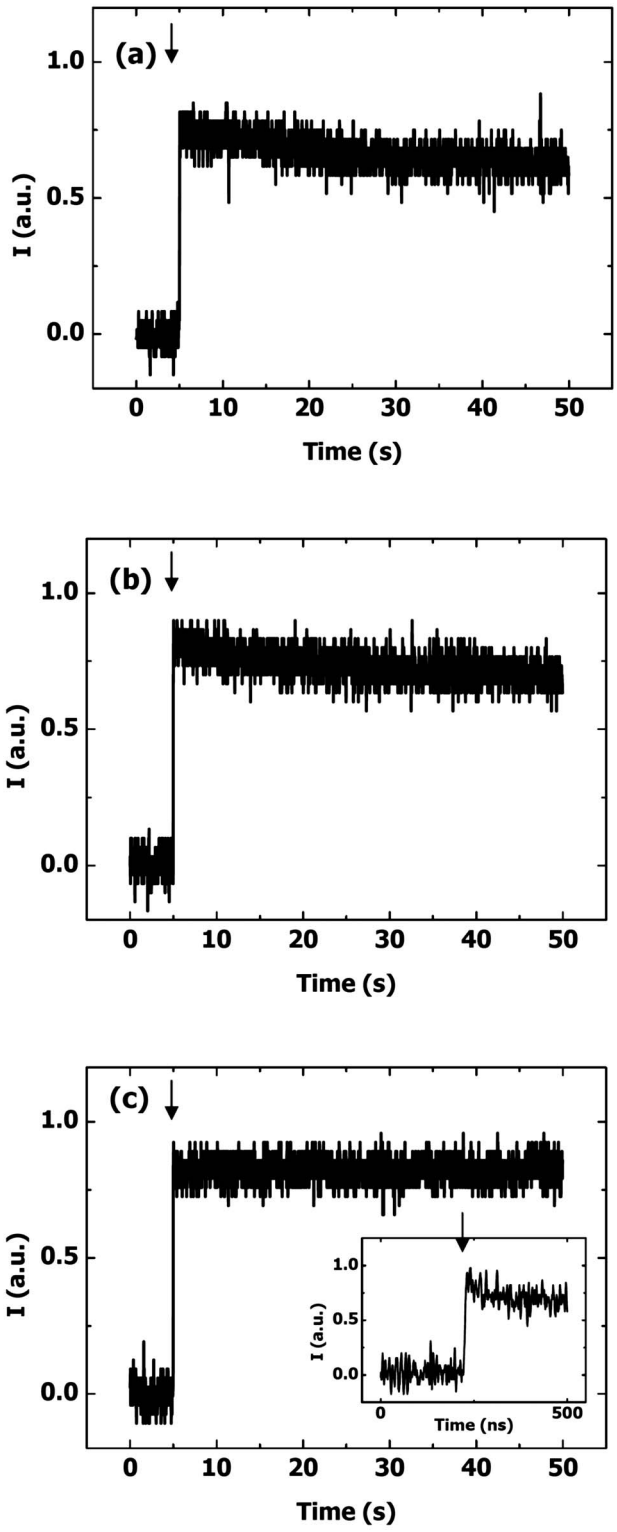

FIG. 5. Intensity transmitted by a polymer film placed between crossed polarizers as a function of time (seconds range) after irradiation with a laser pulse (~500 mJ/cm^2): (a) the statistical copolymer ran-PMMA-Azo20, (b) the terpolymer TER20, and (c) the block copolymer PMMA-Azo20. Inset in shows the same intensity evolution in the nanosecond range. The arrow indicates the time at which the exciting light pulse is triggered.

photoinduced anisotropy. Figure 7 shows the evolution of the transmitted intensity for times up to two days. It can be seen that after the initial increase, photoinduced anisotropy decreases for the three polymers. However, while the signal

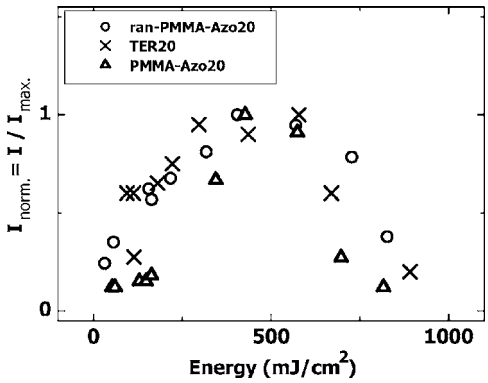

FIG. 6. Intensity transmitted by the polymer films placed between crossed polarizers measured one second after the exciting light pulse, as a function of pulse energy (normalized in each polymer to its maximum transmitted intensity value) for the (○) statistical copolymer ran-PMMA-Azo20, (×) statistical terpolymer TER20, and (△) block copolymer PMMA-Azo20.

completely vanishes for the random copolymers, a stable value of about 50% is retained in the block copolymer after the relaxation period as it can be seen in the inset of Fig. 7(c). This result is qualitatively similar to the one previously observed in the azobenzene homologous homopolymer PC6.[38] The stability of the block copolymer is the best of the three studied architectures. This can be correlated with the segregation of the azobenzene molecules in nanoscopic lamellae observed in the block copolymer. The interaction of neighbor chromophores within the lamella makes the material response close to the one of the homopolymer. In the case of random copolymers, chromophore-chromophore interactions are weaker and the birefringence reached after the excitation pulse relaxes to zero.

Polarization holographic recording has also been explored in films of these three materials. Polarization gratings as described by Nikolova and Todorov only diffract light into ± 1 orders (apart from zeroth order), and the diffracted light is highly polarization selective.[39] Circularly polarized light is fully diffracted into one order, either +1 or −1, depending on the handedness of the incident light polarization. Gratings are recorded in our case by interference of two orthogonally circularly polarized pulses. The time evolution of diffracted light intensity was followed by measuring the first order diffraction (+1) of a circularly polarized 780 nm beam. The ratio between the +1 and −1 orders was also measured just after the pulse to characterize the selectivity of the recorded gratings with respect to reading light polarization.

Figure 8 shows a typical time evolution, in the nanosecond-microsecond range, of the light intensity diffracted in the +1 order by a grating generated using a polarization pattern (single pulse exposure) in the block copolymer. As in birefringence measurements, the diffracted light was too low to be detected in the case of the statistical copolymers with our experimental setup in this time scale. After an initial increase of the diffracted intensity (within few nanoseconds) followed by a slight decrease (within tenths of nanoseconds), no significant variation is observed in the diffracted intensity within the time of this measurement. As in photoinduced anisotropy experiments, an optimum recording energy (giving place to the highest diffracted intensity) is

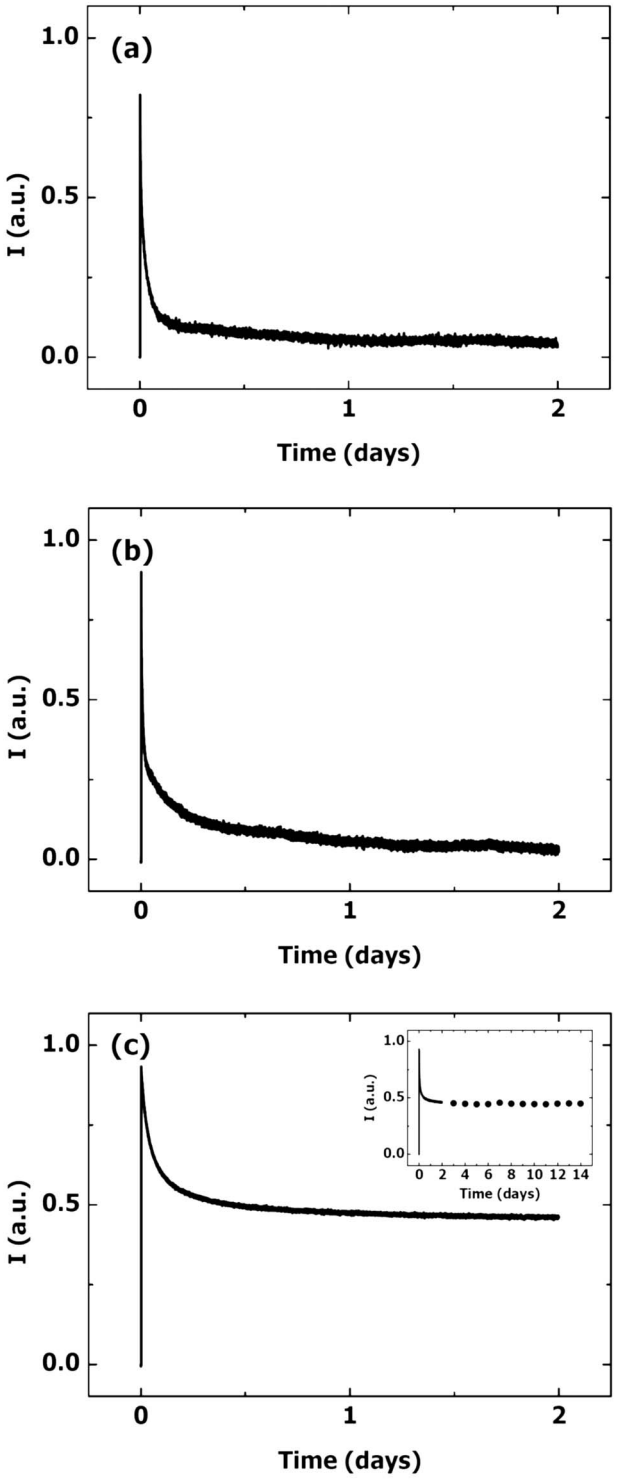

FIG. 7. Intensity transmitted by the polymer films placed between crossed polarizers as a function of time (long term stability): (a) statistical copolymer ran-PMMA-Azo20, (b) statistical terpolymer TER20, and (c) block copolymer PMMA-Azo20. The exciting light pulse is triggered at $t=100$ s. Inset in shows the transmitted intensity measured over two weeks.

identified at about 300 mJ/cm^2 per beam and per pulse. The total energy deposited in the film (twice the beam energy) at the optimum recording energy approximately corresponds to the optimum energy in the birefringence studies (see Fig. 6).

At the optimum recording energy, diffraction efficiency was much higher in the block copolymer film than in the

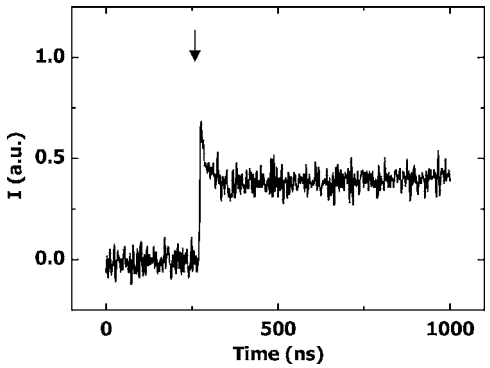

FIG. 8. Diffracted intensity as a function of time (nanosecond-microsecond range) of a sample of the block copolymer PMMA-Azo20 irradiated with a polarization pattern (300 mJ/cm^2 single pulse). A circularly polarized 780 nm laser beam was used as the reading beam. The arrow indicates the time at which the exciting light pulse is triggered.

random copolymer ones (two orders of magnitude), although thickness and absorption spectra were similar for the three polymers. Figure 9 shows the diffraction efficiency stability of the polarization gratings for the three polymers. While the efficiency in the block copolymer reaches a stable efficiency of about 50% of the initial value after one day, it vanishes, almost completely, for the random copolymers after several hours.

The ratio between the +1 and −1 orders at the optimum recording energy was above 200. Thus, the recorded grating shows the features predicted by Nikolova and Todorov for polarization gratings.[39] This result is compatible with our profilometer measurements in which no surface relief grating was observed.

The results on polarization holographic recording show a clear parallelism with those on photoinduced anisotropy described above. This is due to the fact that holographic recording relies on the photoinduction of optical anisotropy along the polarization pattern. Actually, the diffraction efficiency of the +1 order in a polarization grating follows the same dependence on birefringence as the transmitted light between crossed polarizers in the photoinduced anisotropy measurements described above [see Eqs. (1) and (2)].

Holographic recording of polarization gratings with submicron periods (700 nm) has also been carried out in a block copolymer film of about 6 μm thick. The optical absorption of this film at 532 nm is 0.09. Thus, since more than 80% of the incident light is transmitted, we assume that a grating will be recorded through all the volume of the film. With our experimental conditions, we estimated a Q parameter value of 38 and therefore we are in the Bragg regime ($Q > 10$). In fact, we have observed a Bragg diffracted beam coming out from the film. As the Bragg angle is detuned, the diffraction efficiency strongly decreased, indicating that a thick grating was formed. Figure 10 shows the normalized diffraction efficiency as a function of the angular deviation from the Bragg angle. It can be seen from this plot that the angular width at half maximum is 6°. Efficiencies up to 0.5% have been reached in one single pulse. Better angular selectivities can be reached by using ticker films. For this, further dilution of the azo content may be required, for example, by using

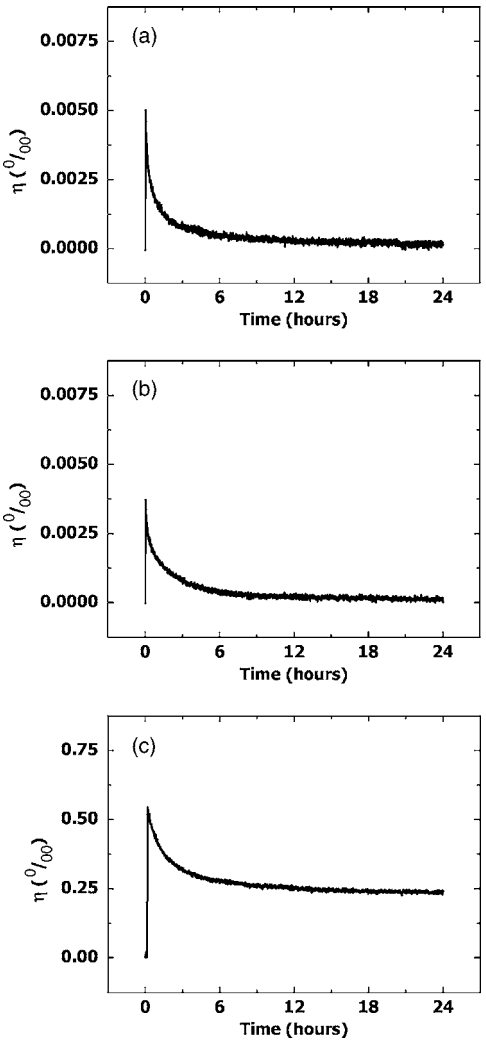

FIG. 9. Diffraction efficiency as a function of time (long term stability) of a sample irradiated with a polarization pattern (300 mJ/cm^2 single pulse): (a) statistical copolymer ran-PMMA-Azo20, (b) terpolymer TER20, and (c) block copolymer PMMA-Azo20. A circularly polarized 780 nm laser beam was used as the reading beam. The exciting light pulse is triggered at $t = 100$ s.

new nanosegregated azobenzene block copolymers with lower relative azobenzene content or blends of block copolymers with other transparent polymers as recording media. Studies on this type of materials are in progress in our laboratory.

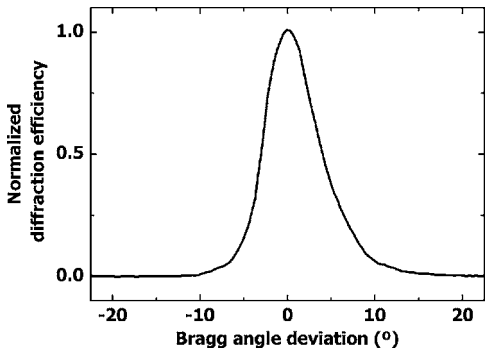

FIG. 10. Normalized diffraction efficiency of a polarization grating as a function of the deviation angle from the Bragg condition. The grating, with a period of 700 nm, was recorded in a block copolymer 6 μm thick film by using a polarization pattern (single pulse exposure).

CONCLUSIONS

We have reported in this paper the pulsed light-induced recording (532 nm, 4 ns pulses) of photoinduced anisotropy and holographic polarization gratings in thin films of polymethacrylates with different macromolecular architectures and a fixed percentage (20 wt. %) of azobenzene side units linked to the main polymer chain. The photoresponse of random and block copolymers containing azobenzene and MMA moieties and statistical terpolymers bearing azobenzene, biphenyl, and MMA units has been compared. Photoinduced anisotropy induced with one single pulse was higher in the case of the block copolymer as compared with the two statistical copolymers. A significant difference in the stability of the recorded anisotropy has also been found. The anisotropy obtained just after the light pulse completely vanishes in a few hours for the statistical copolymers, while a significant stationary value is retained in the block copolymer.

Polarization gratings have been recorded using two orthogonally circularly polarized beams. Larger values of the efficiency (for similar film thickness and recording conditions) are obtained for the block copolymer. Besides, the recorded gratings reach a stationary value for the diffraction efficiency in the block copolymer, while this efficiency drops to zero for the statistical copolymers. The different behavior of the block copolymer can be associated with the chromophore-chromophore interactions within the segregated azo nanodomains that seem to enhance the stability and the photoresponse of the block copolymer. Finally, the recording of polarization gratings with angular selectivities of few degrees has been demonstrated using films of few microns and a grating period of 700 nm.

ACKNOWLEDGMENTS

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